
Best left to leach? Geochemical understanding of waste tips at abandoned metal mines

Alison J. M. Turner¹ Charlotte Braungardt²

¹ *Golder Associates, 1 Havelock Street, West Perth, 6005. Western Australia. aturner@golder.com.au*

² *School of Geography, Earth and Environmental Science, University of Plymouth, Drake Circus, Plymouth. PL4 8AA. United Kingdom. charlotte.braungardt@plymouth.ac.uk*

Abstract

Abandoned mines in the UK offer the opportunity to study the geochemistry of metal mine waste and leachates. This is particularly valuable since findings are based on real data from mature tips (often 100+ yrs old), rather than predictive modelling. A range of research methodology was undertaken to characterise selected waste tips from south west England. The main outcomes of the study were to recognise the complex geochemical equilibrium that exists within waste dumps and the sensitivity of metal and arsenic mobility to pH change. Future management strategies must prioritise this if they are to be successful in reducing the contamination risk to controlled waters.

Key words: metals, mine, ARD, leachate, risk, management, geochemistry, waste rock.

Introduction

Prediction of the quality of drainage waters from waste rock deposits is one of the biggest challenges facing the mining industry. The complexity of chemical reactions and physical mechanisms to consider is overwhelming and yet regulators increasingly demand long-term predictions of water quality hundreds of years into the future before consent for new projects is granted. While sophisticated hydrological and chemical modeling codes can be used for such predictions, they often rely heavily on limited geochemical data and assumptions. It has been recognized for some time that abandoned mines present a problem as a source of pollution but they also provide a valuable resource for the study of mine water discharges and waste rock chemistry. A study was conducted of the magnitude of pollution from mine waste tips at two long-abandoned and contrasting mine sites in south west England. During the study a number of analytical techniques and technical disciplines were employed to investigate the geochemical processes controlling drainage water chemistry. This paper describes some of the most interesting findings from the study and discusses the implications for the management of abandoned mine sites. It also suggests how these lessons may be applied to the design and planning of waste rock facilities at new mines.

Study Sites

Both study sites were abandoned metal mines located in the historical mining area of south west England. The region was extensively mined for a host of metals, principally tin and copper, and was most productive during the mid-19th century. Site 1 was Devon Great Consols, which underwent several phases of operation,

initially underground working for copper and latterly arsenic then some surface reworking and processing of ore for arsenic until its closure in the early 1900's (Booker 1967; Richardson 1995). Site 2 was Wheal Betsy a slightly older mine worked for silver and lead in the 17th and 18th century. Both ore bodies were sulphide deposits and contained appreciable quantities (up to 8% by weight) of chalcopyrite, sphalerite, arsenopyrite, galena, along with an array of associated minerals, largely quartz, pyrite and silicate minerals, both sites had a paucity of carbonate phases.

Stamping, crushing, separation and some roasting of ore was conducted on both sites. Waste deposition was by manual tipping into a number of dumps; it appears that waste was deposited close to the area of processing that created it with little or no consideration of the impact on water or soil quality. In some cases mine waste was used as a construction material for drainage ditches, paths and precipitation launders. Backfilling of mine shafts with waste was also a common method of disposal at the mines.

Following mine closure the sites have been publically accessible and despite the contamination risks, have been frequented by walkers, cyclists, motorcyclists and off-road vehicles. The tips have been particularly favored by mountain bikers and off-road vehicles which have contributed to the high erosion rates of some tips. Although difficult to directly measure there is strong evidence for ongoing erosion from the distribution of characteristic tip material down gradient and deep erosion gulleys in the side of the tips.

In recent years the sites have been recognized as being of historical importance and have been afforded various levels of management and protection. Devon Great Consols is among a number of mines given world heritage site status by UNESCO in 2006, under the banner of "Cornish Mining" (CMWH 2010). As such, measures have been implemented to encourage and manage public access. The engine house at Wheal Betsy is owned and maintained by the National Trust and this site belongs to the regional water authority and lies on the boundary of Dartmoor, a recognized National Park.

Methods

The surface and shallow groundwater drainage at each site was characterized for master variables, water chemistry and flow. This included the determination of metal and metalloid concentrations by ICP-MS and ICP-OES, determination of anions by IC. Sample collection and treatment was conducted in accordance with best practice guidelines (INAP 2012, Price 2009) and analysis conducted in an accredited facility with appropriate quality control procedures in place.

Samples of the mine waste were recovered from a number of areas of waste at each site, again adhering to best practice guidelines. The samples were taken from the shallow sub-surface below the outermost weathered crust or root zone, where present.

Selected samples were sieved to sub-4mm. Composite samples were created to be representative of four discrete waste tips found at the sites. These were the Wheal Anna Maria and Cinders dumps at Devon Great Consols 1(WAM, CIND) and north

and south tips at Wheal Betsy (WBN, WBS). The samples were subjected to static and kinetic leach tests. The exact method may be found in Turner *et al.* (2009).

The composite material and selected samples were characterized for particle size, and mineralogy by powder XRD and SEM-EDX. Finally information on rainfall, wind and sun exposure, stream locations, catchment areas, vegetations and topography were gathered into a GIS database in order to thoroughly characterize each of the sites.

Results and Discussion

Mine Waste Content

As may be expected, mine waste contained a wide variety of eco-toxic metals and metalloids associated with sulphide-hosted mineral deposits (Figure 1). Waste tip material contained a small proportion (<5%) of primary sulphide ore minerals, and Pb, Cu, Zn, and As were mostly associated with abundant secondary Fe phases and clays such that it was the stability of these phases that controlled contaminant release.

SEM observations of the texture and abundance of the sulphide minerals within the mine waste suggested the preferential weathering of iron pyrite and metal sulphides with respect to arsenopyrite which was the most persistent primary sulphide phase in all the waste tips. The mineralogical analysis conducted on the two major areas of waste at Devon Great Consols also revealed them to be of comparable bulk mineralogy and elemental composition, particularly for As and Cu, the major contaminants of interest at the site.

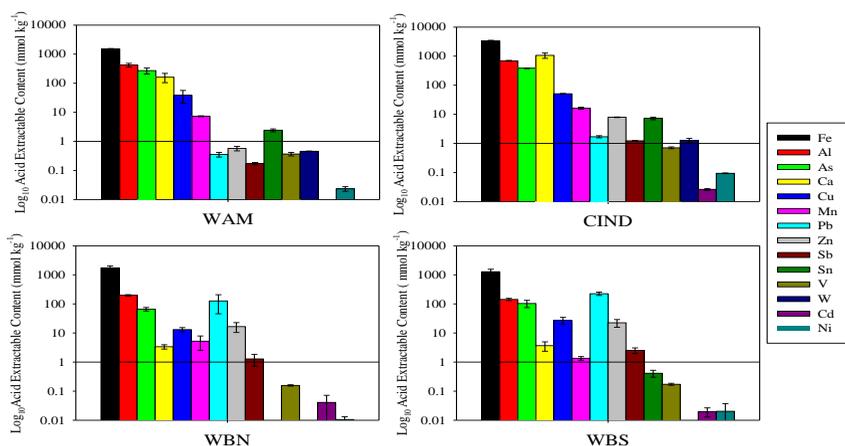


Figure 5 Acid extractable metals and metalloids determined by aqua regia digestion for composite mine waste samples used in batch and column experiments. Bars represent mean of triplicate results, error bars represent +/- 1 s.d. Note logarithmic scale on y-axis.

Table 1: Summary of mean acid extractable content for Cu, Zn, Pb and As from selected mine wastes. All units mmol kg⁻¹. Highest result for each element in bold.

	Cu	Zn	Pb	As
WAM	35.8 ± 18	0.572 ± 0.10	0.354 ± 0.07	272 ± 65
CIND	50.8 ± 1.1	7.93 ± 0.20	1.69 ± 0.15	383 ± 8.2
WBN	13.1 ± 2.2	16.6 ± 6.1	126 ± 80.5	66.4 ± 9.0
WBS	27.0 ± 7.5	22.4 ± 6.6	224 ± 29.3	104 ± 29

Water Quality

During this study (2007-2009), leachates were observed to issue from the mine waste tips at Devon Great Consols following periods of heavy short term rainfall (> 45 mm in 7 days) due to the formation of a perched water table within the waste. The concentrations of dissolved metals in the issuing waters were very high compared to environmental quality standard (EQS) values and highly variable e.g. Cu in drainage from Wheal Anna Maria (WAM) tip ranged from 135-387 µmol L⁻¹, respectively. Drainage waters emanating the cinders, and WAM waste tips were generally oxic and in excess of EQS values for dissolved Al, Cu, Zn, Ni, Cd, Mn, Fe and As.

The hydrology of the Wheal Betsy site was much simpler than at Devon Great Consols, with a short migration pathway (<10m) from tips to the receiving watercourse. Groundwater table and stream flow were highly reactive to short-term rainfall patterns and concentrations of dissolved contaminant metals were increased in the brook during wet surveys. The receiving watercourse failed long term EQS for Al, Zn, Cu, Pb, and Cd during all surveys. The highest exceedance was for dissolved Cd (0.018 µmol L⁻¹, equal to 250 x EQS), dissolved Mn (11.0 µmol L⁻¹, equal to 87 x EQS) and dissolved Zn (3.9 µmol L⁻¹, equal to 55x EQS). Concentrations and fluxes of dissolved metals increased with increased rainfall and this was attributed to higher water tables in the base of the waste tips.

Fractional release of elements from the mine waste was generally observed in column and field leachates when compared to the mineralogical assays of the solids. However at low concentrations (<5 µmol L⁻¹), selective retention via metal adsorption onto secondary Fe phases was inferred from column release curves in the order of affinity of Pb>Cu>Mn>Zn>Cd> Ni.

Principle component analysis demonstrated that areas of waste exhibited distinct geochemical signatures. The difference in dissolved As and Cu (Figure 2) between the two DGC tips was striking given the comparable As and Cu content within the solid matrix (Figure 1), similar particule size, their close proximity to one another (<20 m). This was attributed to the sensitivity of metal and As behaviour at the solid-solution interface with respect to pH. Leachate pH from the cinders waste was consistently higher (pH 5.0-5.4) than for WAM leachate (pH 3.2-4.0), which was sufficient to transform the sorption properties of the soils. Arsenic concentrations were also higher in the field (up to 380 µmol L⁻¹, pH 5.0-5.3) than in the laboratory experiments (up to 41 µmol L⁻¹, pH 4.0-4.5), further reflecting the greater mobility of oxyanions at higher pH values. Conversely, for some metals and

in particular Pb, concentrations were lower in the field, (up to 2.8 $\mu\text{mol L}^{-1}$ pH 3.2-5.6) compared to laboratory leachates (up to 81 $\mu\text{mol L}^{-1}$, pH 1.9-2.6).

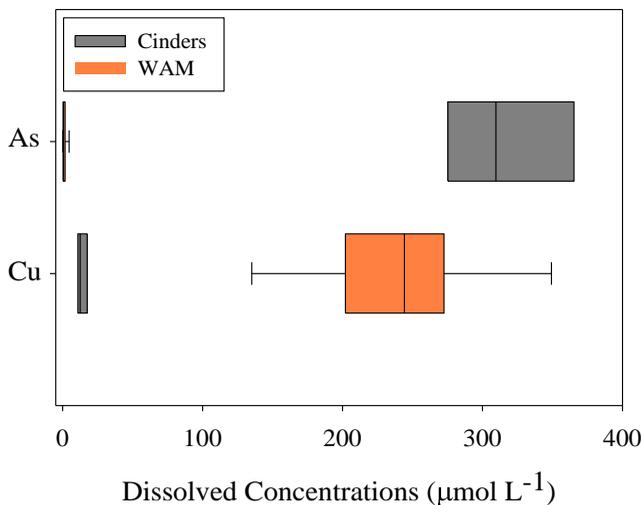


Figure 6: Contrasting water quality data for dissolved copper and arsenic emanating from the cinders and WAM waste tips at Devon Great Consols mine site.

Working with Nature - Enhancing Natural Attenuation

When mine waste is located far from a receiving watercourse the dividing area acts as a buffer, effectively filtering suspended solids and dissolved metal(oids) from discharge waters. This was shown clearly by the reduction in surface drainage concentrations in the final collection drain at Devon Great Consols, compared to the concentrations leaving the tips approximately 350m up gradient. Upon leaving the final collection drain at the site, concentrations of most metals had fallen by at least an order of magnitude. Furthermore As had fallen from some of the highest values recorded in the region for oxic waters, to consistently below the freshwater EQS value across all sampling conditions ($0.23 \pm 0.05 \mu\text{mol L}^{-1}$). The intermediate ground comprised a tortuous complex of leats and gulleys flowing through an area of mixed forest (deciduous and coniferous). This was compared to Wheal Betsy where the very short path (<20 m) across over and through thin acidic soils with sparse vegetation resulted in no observable attenuation before entering the receiving watercourse. As a result dissolved contaminants migrated further downstream from the site in the fast flowing waters of the receiving watercourse.

For a buffer to work effectively, transported waters must remain oxic. Development of reducing conditions will enhance secondary Fe-oxide phase dissolution and release associated metals and As. This is particularly important in the case of As where speciation is dependent on redox condition and mobility of the reduced species As(III) is greater than As(V). The capacity for iron oxides to adsorb As(V) is well documented in circum-neutral and acidic waters (Shand et al.

2007) and adsorption reactions are generally considered the most important control on the concentration of dissolved arsenic in groundwater environments. As (V) is generally mobile (as dissolved H_3AsO_4 and H_2AsO_4^-) only at $\text{pH} < 3.5$ in a narrow range of Eh (Cheng et al. 2009). Waters which discharge from underground workings or waters which migrate slowly in the subsurface tend to be rich in dissolved Fe due to isolation from the atmosphere. A rapid but tortuous pathway and an introduced source of dissolved Fe, perhaps from a nearby adit discharge are likely to enhance natural attenuation.

Although competitive sorption effects are small in magnitude compared to overall concentrations they may prove to be an important consideration when implementing remedial measures. Sorption of one metal may cause the preferential release of another with lower binding energy to mineral surfaces. For example Pb was highly abundant in the waste from Wheal Betsy but remained largely immobile under field conditions, but lower pH in laboratory experiments triggered release. Cu and Pb compete for binding sites on Fe-oxides (Baker, 1980), so in the presence of dissolved Pb, the natural attenuation of Cu is suppressed. Potentially, a release of dissolved Pb may be short lived in the environment but could result in a spike of the more mobile metal, here Cu, in downstream waters. pH exerted a very strong control on the mobility of all the studied elements. This was shown by differences in laboratory test results compared to field drainage. Higher mobility was observed for all cationic species as pH decreased, while anionic As was more mobile at higher pH.

Amendments applied to the waste or discharge waters must be carefully considered if they adjust the pH of the solid solution interface. At Devon Great Consols, the cinders tips had the largest copper content but the WAM tips release more dissolved Cu. This was attributed to the higher intrinsic buffering of the cinders waste which produces a higher pH in the waste porewaters (pH 4.0-4.5), compared to WAM waste (pH 2.4-3.7). In the cinders waste, As is released in very high concentrations in the field ($294 \mu\text{mol L}^{-1}$) where pH is highest (pH 5.0-5.4). In the laboratory experiments the pH of the cinders waste was lower and maximum As release was 10 x lower than observed in the field. Higher pH increases the cationic sorption capacity of the waste. Amending WAM tip waste with lime solution (CaCO_3 for example), may raise the pH and increase the retention of dissolved Cu to the solid phase. But the low pH is beneficial for the retention of anionic As species and therefore raising the pH could trigger release of As instead. Conversely reduced pH in the cinders waste would reduce the As flux but could result in a higher flux of Cu than currently observed from the WAM waste. Circumstances which could result in reduced pH might be the disturbance of the tip and inundation of O_2 to oxidise unweathered pyrites within the waste.

Conclusions

Overall, the waste tips at abandoned mines in the Tamar catchment have been shown to be major contributors to the pollutant flux of metals and metalloid entering watercourses. They are small by international standards, but contain high concentrations of metals and arsenic and are often in close proximity to watercourses subject to water quality regulations under the Water Framework Directive (2000/60/EC). Cautious estimates of the metal flux arising from waste

tip drainage have shown that they are of the same magnitude as known adit discharges and therefore are worthy of management.

The variability in leachate pH from mine waste in the field and laboratory, and the effect observed in contaminant mobility as a result, highlights two important cautionary notes. Firstly, that unless laboratory leaching experiments are able to replicate field pH, the the results may be highly inaccurate and caution should be used when using them as input values for water quality predictions. Secondly that assesment of leaching potential based on the properties of the solid matirx alone, as is common place in early-phase prediction studies, is highly unlikely to be able to predict the pH of drainage to the level of accuracy required to adequately predict sorption behaviour. Put simply, validation against field measurements must be undertaken for laboratory data to be meaningful.

However, the misrepresentitive laboratory leaching experiments have served to show that there is much greater potential for contaminant release from the waste material than is recorded in the field. The fine balance of chemical reactions, water transport and physical erosion combine to produce a characteristic leachate composition for each area of waste. Disturbance of the waste will upset this balance and the most likely outcome is enhanced leaching and sediment transport unless remediation schemes are very carefully implemented. There is no "one-size fits all" solution, the variability between tips is too great, and this makes appropriate treatment prohibitively expensive. Therefore passive management and monitoring strategies provide the lowest risk and most cost effective method of stewardship for these sites and others like them in the United Kingdom, particularly those in similar geological settings (e.g. south west England and Wales).

The most productive short-term action would be to control access and reduce human exposure to potentially harmful elements within the waste. Measures could also be taken to enhance the stability of the tips, thereby reducing the suspended load of contamination entering streams and reduce the exposure of fresh mineral surface to weathering. The least invasive treatment would be to encourage natural accession of vegetation from bryophytes (nutrients from air, resistant to toxicity of waste) to nitrogen fixers (gorse and heather) to grasses and shrubs. Vegetation of the tips would increase stability, and reduce water movement and inhibit O₂ ingress, all favorable for the reduction of pollutant flux leaving the tips and a common design strategy for new waste rock facilities. Destructive or invasive measures should also be avoided because disturbance the tip material is an integral part of the industrial archaeology of the United Kingdom and the mining industry as a whole. Furthermore, they also provide a niche and relatively undisturbed environment for flora and fauna in areas under increasing pressure from human development.

Acknowledgements

I would like to thank Ben Williamson at Cambourne School of Mines for his assistance with SEM-EDX interpretation.

References

- Booker, F. (1967). *The Industrial Archaeology of the Tamar Valley*. Newton Abbot, David & Charles Ltd. pp 303 pp 130
- Cheng, H., Hu, Y., Luo, J., Xu, B. and Zhao, J. (2009). Geochemical processes controlling fate and transport of arsenic in acid mine drainage (AMD) and natural systems. *Journal of Hazardous Materials*. 165 (1-3) pp 13-26.
- CMWH.(2010). "Cornish Mining World Heritage." Cornwall Council Accessed 12th April 2010. Available on the world wide web at: <http://www.cornish-mining.org.uk/project/aboutus.htm>.
- INAP.(2012). "Global Acid Rock Drainage Guide (GARD Guide)." International Network for Acid Prevention. Accessed 10/05/2012. Available on the world wide web at: <http://www.gardguide.com/>.
- Price, W. A. 2009. Prediction manual for Drainage Chemistry from Sulphidic Geologic Materials. Smithers, British Columbia: CANMET Mining and Mineral Sciences Laboratories.
- Richardson, P. H. G. (1995). *Mines of Dartmoor and the Tamar Valley after 1913*. Torquay, Devon Books. pp 160 pp 50-52
- Shand, P., Edmunds, W. M., Lawrence, A. R., Smedley, P. L. and Burke, S. (2007). The natural (baseline) quality of groundwater in England and Wales. Research Report No. RR/07/06 British Geological Survey
- Turner, A., Braungardt, C.B., Worsfold, P.J., Rieuwerts, J., Williamson, B., Potter, H. (2009) Dynamic up-flow percolation tests - a model for mining waste leachate generation. International Mine Water Association and The Water Institute of Southern Africa. Proceedings of the International Mine Water Conference, 19-23 October 2009, Pretoria, South Africa, p. 858-867. ISBN: 978-0-9808683-5-3.